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Effect of CeO₂ Presence on the Electronic Structure and the Activity for Ethanol Oxidation of Carbon Supported Pt

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Abstract: Pt/CeO₂/C electrocatalysts in different compositions were prepared and their structural characteristics and activities for ethanol oxidation in alkaline media were evaluated. In the presence of CeO₂, an increase in the platinum particle size was observed. XANES measurements indicated that the Pt d-band vacancies increased with increasing CeO₂ amounts. For the first time, the decrease in electro activity was described to an electronic effect for high CeO₂ contents. The dependence of the activity for ethanol oxidation on CeO₂ content went to a maximum, due to the counteracting bifunctional and electronic effects of the metal oxide.

Keywords: platinum; ceria; ethanol oxidation; fuel cell; electrocatalyst

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1. Introduction

The development of effective alkaline anion-exchange membranes led to a boost in alkaline fuel cell (AFC) research [1]. Among AFCs, alkaline direct alcohol fuel cells (ADAFCS) seem the most promising for use as portable power sources [2]. The easiness to store and transport makes liquid fuels, such as methanol and ethanol, more suitable for their use in fuel cells than hydrogen. Additionally, ethanol can be obtained in a large amount from biomass and having lower toxicity than methanol. Palladium and platinum are the most active metals for the ethanol oxidation reaction (EOR), in both media—acid and alkaline [3]. In an attempt to increase the EOR activity, various metal oxides were added in Pt or Pd [3]. Melchionna et al. [4] reported the use of C–CeO₂ composites as supports of Pt and Pd catalysts for the anodic oxidation of alcohols, for applications in direct alcohol fuel cells. Carbon in ceria-based composites remarkably facilitates electron transfers, provides high conductivity and high surface area, and improves stability. It was observed that the presence of ceria improves the catalytic activity for alcohol oxidation of Pt/C and Pd/C, also if the role of CeO₂ in Pd- or Pt–CeO₂/C was not fully understood. The improved activity was ascribed to the promoted CO removal by oxidation to CO₂ catalyzed by the ceria, avoiding precious metal poisoning, although ceria could have a more complex function [5]. There is a common opinion that the electro-oxidation of ethanol, by Pd catalysts is catalyzed by Pd–OH_{ads} species formed after adsorption of the hydroxide, and higher concentrations of Pd–OH_{ads} lead to faster fuel conversion [6]. The addition of CeO₂ increases the oxidation rate of Pd to Pd–OH_{ads}, with the formation of a high amount of active species and, therefore, improves performance in direct ethanol fuel cells [7].

Many studies focused on the effect of the addition of CeO₂ to Pt/C on electrochemical oxidation of methanol and ethanol [8]. Different factors determine the performance of Pt/CeO₂ catalysts, related both to platinum, such as Pt precursor kind [9], Pt loading [10], Pt nanoparticle dispersion [11], size [12] and shape [13], and Pt electronic state [14], and to ceria, such as CeO₂ morphology [15–17] and amount of CeO₂ oxygen vacancies [18,19].

Generally, the addition of CeO₂ to Pt results in a higher activity, and the electro activity of Pt/C–CeO₂ for low molecular weight alcohol oxidation on ceria content goes through a

maximum [4]. Certain characteristics of cerium oxide, such as, oxygen storage capacity may be responsible for the increase in activity, facilitating the CO oxidation. Compared to acid media, for the EOR on Pt/C-CeO₂ in alkaline media there are few works [20–26]. First, Xu et al. [20–22] investigated the EOR activity in alkaline media of Pt-CeO₂/C catalysts with various amount of CeO₂, prepared by H₂PtCl₆ reduction on CeO₂/C powder. The presence of CeO₂ improved the EOR activity of Pt, passing through a maximum at a Pt/CeO₂ weight ratio in the range 1.3–2.0. Then, Sedighi et al. [23], by electrochemical impedance spectroscopy (EIS) measurements, found that the transfer charge resistance (R_{ct}) of Pt-CeO₂/CNT in 1.0 M KOH and 1.0 M CH₃CH₂OH solution at 0.1 V vs. Ag/AgCl is considerably lower than that of Pt/CNT, showing that the presence of CeO₂ positively affects ethanol oxidation in alkaline media. Finally, Katayama et al. [24] compared the effect of cerium oxide presence on the activity for ethanol oxidation of platinum in acid and alkaline media; only in alkaline medium was a positive effect observed. The role of CeO₂ in Pt-CeO₂/C and the presence of a maximum, however, is not fully understood. Thus, to better understand the effect of CeO₂ content on the EOR activity of Pt in alkaline medium, Pt/CeO₂/C catalysts in different compositions were prepared, then their activity for EOR was evaluated by cyclic voltammetry (CV), linear sweep voltammetry (LSV), chronoamperometry (CA) and repetitive potential cyclic (RPC) measurements. In situ X-ray Absorption Spectroscopy (XAS) experiments were in the Brazilian Synchrotron Light Laboratory (LNLS) and the electronic effect related with CeO₂ presence were discussed.

2. Results and Discussion

The EDX average compositions of the Pt/CeO₂/C electrocatalysts was shown in Table 1, demonstrating agreement with the nominal compositions.

Table 1. EDX and TGA mass compositions, and EDX and XPS atomic compositions of Pt/CeO₂/C catalysts.

Material	(Pt+CeO ₂) wt%/Nom.	CeO ₂ wt%/Nominal	CeO ₂ wt%/EDX	(Pt+CeO ₂) wt%/EDX	(Pt+CeO ₂) wt%/TGA	Pt wt%/EDX	Pt/Ce at%/EDX
Pt/C	20	-	-	23	22	23	100/0
Pt/4CeO ₂ /C	19	4	4	21	21	17	79/21
Pt/6CeO ₂ /C	21	6	6	21	18	15	69/31
Pt/8CeO ₂ /C	23	8	8	23	27	15	62/38

The thermogravimetric analysis (TGA) was carried out on Pt/C and Pt/CeO₂/C catalysts. TGA weight loss curves of Pt/C and Pt/CeO₂/C catalysts are shown in Figure 1. For Pt/C, the region between 25–360 °C is due to the removal of water and formic acid going from the synthesis of the catalysts [27]. The region from 360 to 520 °C is related to carbon oxidation potentiated by Pt that acts as a catalyst. For temperatures >520 °C where constant weight is observed we can determine the weight of the Pt and CeO₂ species presents. The sum of Pt and CeO₂ content (wt%) in the catalysts by thermogravimetric was similar to that obtained by EDX analysis (Table 1). An increase in the onset carbon combustion temperature (T_{onset}) in the presence of CeO₂ can be observed in Figure 1. T_{onset} enhancement could be due to an increase of Pt particle in the presence of CeO₂, as shown later.

The XRD patterns of the Pt/CeO₂/C and Pt/C and, for comparison, of CeO₂ alone, are shown in Figure 2. The XRD pattern of Pt/CeO₂/C and Pt/C catalysts showed the characteristic peaks of the face centered cubic (fcc) crystalline Pt and show the first peak related to the (002) phase of the hexagonal structure of carbon. No appreciable shift of these diffraction peaks in the Pt/CeO₂/C catalysts with respect to those of Pt/C was observed indicating no alloy formation. The presence of CeO₂ reflections were observed in the XRD patterns of the Pt/CeO₂/C catalysts. Table 2 shows the average crystallite sizes determined using the Sherrer equation. In the presence of CeO₂, an increase of the crystallite size was observed compared to Pt catalyst alone.

Figure 1. Thermogravimetric analyses of Pt/C and Pt/CeO₂/C catalysts. The measurements were performed in air atmosphere up to 1000 °C with a heating ramp of 10 °C min^{−1}.

Figure 2. XRD patterns of Pt/C and Pt/CeO₂/C catalysts and CeO₂ alone.

Table 2. Crystallite size (dc) by XRD, and number average particle size (dn), Gaussian average particle size (dG) and distribution asymmetry index (AG) by TEM and roughness factor (RF) by CV (H₂) of Pt/CeO₂/C and Pt/C catalysts.

Material	dc nm	dn nm	dG nm	AG	ECSA m ² g ^{−1}
Pt/C	3.1	4.32	4.27	0.01	45
Pt/4CeO ₂ /C	5.0	5.23	4.64	0.11	18
Pt/6CeO ₂ /C	6.9	6.07	5.63	0.07	9
Pt/8CeO ₂ /C	5.9	5.98	5.52	0.08	13

Figure 3a–d shows TEM images and histograms of the Pt/CeO₂/C and Pt/C catalysts. For all catalysts prepared, the Pt nanoparticles were homogeneously distributed on the support. In the hypothesis—that all the observed particles are Pt, the Pt particle size distribution was in the range 2.5–6.5 nm for Pt/C and 1.2–14.5 nm, 2.8–12.0 nm and 1.8–12.0 nm for

Pt/4CeO₂/C, Pt/6CeO₂/C and Pt/8CeO₂/C catalysts, respectively. That is, in the presence of CeO₂, the Pt particle size distribution was in a broader range. On the other hand, if the observed particles are both Pt and CeO₂, the tail of the histograms in the high particle size range could be ascribed to ceria particles.

Figure 3. Images and histograms of particle size distribution of Pt/C (a), Pt/4CeO₂/C (b), Pt/6CeO₂/C (c), and Pt/8CeO₂/C (d).

The Gaussian fitting was used to determine the average particle size in the histogram of Pt/C and average Gaussian Pt particle size (dG), reported in Table 2. However, the particle size histograms of Pt/CeO₂/C catalysts showed an asymmetrical TEM distribution. The number averaged particle size (dn) have been calculated using Equation (1):

$$d_n = \frac{\sum n_k n_k d_k}{\sum n_k} \quad (1)$$

where n_k is the frequency of occurrence of particles with size d_k . Table 2 shows the d_n values calculated. The low AG values indicate that asymmetry increases, with observed for Pt/C indicates a uniform particle size distribution. The remarkably higher AG value of Pt/CeO₂/C catalysts than that of Pt/C, as shown in Table 2, indicates a high positive asymmetry. Summarizing, in the presence of CeO₂ carbon supported platinum particles with higher size (d_n) and wider and more asymmetrical (AG) size distribution were obtained with respect to those synthesized without CeO₂.

To determine the oxidation states and surface composition, XPS analysis was carried out on the Pt/CeO₂/C and Pt/C catalysts. Figure 4 presents the XPS spectra of the Pt 4f regions for all catalysts and Ce 3d regions for Pt/CeO₂/C. The XPS spectrum relative

to Ce, O, C and Pt, with their corresponding photoelectron peaks Ce3d, O1s, C1s, and Pt4f are reported in Supplementary Material (Figure S1), showing the long scan. Table 3 lists the assignments of the deconvoluted spectra to various oxidation states and their relative amount.

Figure 4. High-resolution XPS scan of Pt 4f and Ce 3d of Pt/C and Pt/CeO₂/C catalysts.

Table 3. Binding energy values of Pt/CeO₂/C and Pt/C catalysts, with the relative % of different oxidation states indicated in parenthesis and the XPS atomic compositions.

Catalyst	Pt(0) 4f _{7/2}	Pt(II) 4f _{7/2}	Pt(IV) 4f _{7/2}	Ce(III) 3d _{5/2}	Ce(IV) 3d _{5/2}	Pt/Ce at% XPS
Pt/C	71.3 (43)	72.7 (47)	74.4 (10)	-	-	100/0
Pt/4CeO ₂ /C	71.1 (49)	72.7 (43)	74.4 (8)	885.3 (39)	882.6; 888.5; 915.7 (61)	88/12
Pt/6CeO ₂ /C	71.4 (43)	72.7 (43)	74.4 (15)	884.8 (34)	882.9; 888.7; 915.9 (66)	67/33
Pt/8CeO ₂ /C	71.3 (43)	72.7 (45)	74.4 (12)	884.7 (33)	883.0; 888.8; 916.0 (67)	57/43

According to the results of XRD measurements, the XPS no indication of alloy formation, these results do not show considerable shift of Pt 4f binding energies (BEs) in Pt/CeO₂/C catalysts and no change in the relative amount of Pt chemical states than that of Pt/C (71.3 eV) was observed. The Ce(IV)/Ce(III) ratio was ca. 65/35 for all the Pt/CeO₂/C catalyst. Table 3 presents the surface composition of Pt/CeO₂/C catalysts obtained by XPS measurements. By comparison of EDX and XPS compositions for low Ce content Pt segregation takes place, while for high Ce content Ce segregation occurs.

The CV curves in a NaOH solution for Pt/C catalysts are shown in Figure 5. The hydrogen desorption region was utilized for determined the Pt electrochemical surface area (ECSA), following the same procedure described in ref. [28]. The values of ECSA are reported in Table 2. As can be seen in Table 2, the ECSA of all Pt/CeO₂/C catalysts was lower than that of Pt/C, essentially due to the increase of particle size. Moreover, the presence of CeO₂ can partially block Pt active sites.

Figure 5. Cyclic voltammograms of Pt/C and Pt/CeO₂/C catalysts in 0.1 mol L^{−1} NaOH under Ar at room temperature and a scan rate of 50 mVs^{−1}.

XANES measurements were carried out on Pt/CeO₂/C and Pt/C catalysts to evaluate the electronic state of the Pt atoms. Figure 6a,b, shows the XANES spectra at the Pt LIII edge at 0.6 and 0.8 V vs. RHE for these electrocatalysts. The absorption at the Pt LIII edge (11.564 eV) corresponds to the 2p_{3/2}–5d electronic transitions and the integrated intensity of the first Lorentzian (white line) is related to the Pt d-band vacancies. The intensity of the white line for Pt/C is mostly higher than that of CeO₂ containing catalysts (Figure 6). This is due to the higher active area, that is, the higher number of Pt active sites in Pt/C than that in Pt/CeO₂/C catalysts. However, normalizing the white line by the active area, apart from 4 wt% and 6 wt% Pt/CeO₂/C at 0.6 V vs. RHE, the integrated intensity of the white line of CeO₂ containing catalysts was higher than that of Pt/C (Table 4).

Figure 6. XANES Pt LIII absorption for Pt/C and Pt/CeO₂/C catalysts in 0.1 mol L^{−1} at 0.6 V (a) and 0.8 V (b) vs. RHE. Inset: white line magnitude in the range 11,560–11,576 eV.

The lower value of Pt/4CeO₂/C and Pt/6CeO₂/C catalysts than that of Pt/C is related to a particle size effect, as for $d_n \leq 5$ nm Pt d-band vacancies decrease with increasing particle size [29,30]. A remarkable increase of the Pt white line in the presence of CeO₂ was observed also by He et al. [31]. The comparison of the Pt LIII XANES patterns at

0.6 and 0.8 V vs. RHE showed an increase in the intensity of the Pt LIII white line with increasing the potential for the Pt/CeO₂/C, is related to the increase in oxygenated species on the surface of Pt [32]. Figure 7a–c shows the CV, LSV, and CA curves for EOR for the Pt/CeO₂/C and Pt/C catalysts with the current density normalized by the ECSA.

Table 4. Integrated intensity of the Lorentzian corresponding to the first maximum in the XANES spectra.

Catalyst	Area (a.u.)	
	0.6 V vs. RHE	0.8 V vs. RHE
Pt/C	5.69	5.68
Pt/4CeO ₂ /C	5.56	5.69
Pt/6CeO ₂ /C	5.62	5.73
Pt/8CeO ₂ /C	5.79	5.80

Figure 7. Cyclic voltammetry (a), linear sweep voltammetry (b), and chronoamperometry at 0.6 V vs. RHE (c), curves for ethanol oxidation for the Pt/CeO₂/C and Pt/C catalysts with the current density expressed in terms of the ECSA. Inset (c): histogram of the steady state current density. Dependence of $J_{\max}$ by LSV (d), and J_{ss} by CA (e), on CeO₂ content on the catalyst surface.

The maximum current density ($J_{\max}$) by CV and LSV and the steady state current density (J_{ss}) by CA of all Pt/CeO₂/C catalysts, except the J_{ss} of Pt/8CeO₂/C, were higher than Pt/C. A dual-path mechanism for the alcohol oxidation reaction in alkaline media was proposed as [33]:

In the hypothesis that the path (3) is the main reaction path, the EOR on Pt in alkaline media according to the bifunctional mechanism follows the reactions [33,34]:

The chemical reaction given by Equation (7) is the rate-determining step. The adsorbed $\text{CH}_3\text{CO}_{\text{ads}}$ on the Pt catalyst, however, reduces Pt active sites and lead to the reduction of EOR. The higher activity of Pt/CeO₂/C has to ascribe to the synergistic effect between Pt and CeO₂ through the bifunctional mechanism. For the Pt/CeO₂/C catalysts the concentration of OH_{ads} species on the catalyst surface increase, according to Equation (9), and supports the EOR by $\text{CH}_3\text{CO}_{\text{ads}}$ removal and acetaldehyde oxidation to acetic acid:

The dependence of J_{max} by LSV and J_{ss} by CA on CeO₂ content on the catalyst surface is shown in Figure 7d: an increase of J_{max} and J_{ss} by addition of 4 wt% CeO₂ can be observed in Figure 7e, then J_{max} and J_{ss} decreased with further increase of CeO₂ content in the catalyst. The J_{max} obtained at 0.8 V vs. RHE is not useful for an evaluation of the material as an DEFC anode, the J_{ss} obtained at 0.6 V vs. RHE is a result that suggest that Pt/4CeO₂/C is the best anode catalyst for the use in DEFC.

In previous works, the decrease of the activity for methanol [4,35,36] and ethanol [21,22] oxidation of Pt/CeO₂/C catalysts for high CeO₂ contents was ascribed to the increase in the anode resistivity with increasing the amount of the semiconductor CeO₂. However, the increase in the affinity of OH chemisorption on Pt occurs with the increase in Pt d-band vacancy [29,30]: the subsequent coverage of Pt atoms with oxygenated species can lead to a decrease in the ethanol oxidation activity. In this regard, the decrease of the EOR activity of Pt for methanol [37–39] and ethanol [28] oxidation, with decreasing the particle size, was explained with the increase of the adsorption strength of oxygenated species on Pt with decreasing Pt particle size. On this basis, we can suppose that the decrease of EOR activity with increasing CeO₂ content could be due to the increase of Pt d-band vacancy. The dependence of the $A_{\text{PtCeO}_2/\text{C}}/A_{\text{Pt/C}}$ ratio, where $A = J_{\text{ss}}$ (CA, 0.6 V vs. RHE) and J_{max} (LSV, 0.8 V vs. RHE) on Pt LIII white line integrated intensity is shown in Figure 8.

Figure 8. Dependence of the $A_{\text{PtCeO}_2/\text{C}}/A_{\text{Pt/C}}$ ratio, where $A = J_{\text{ss}}$ (CA, 0.6 V vs. RHE) and J_{max} (LSV, 0.8 V vs. RHE) on Pt LIII white line integrated intensity.

The data are strongly correlated, showing a negative linear dependence of both J_{ss} and J_{max} on Pt LIII white line intensity and clearly indicating that the reduction of J_{ss} and J_{max}

with increasing CeO₂ content has to be ascribed to the enhancement of Pt site coverage with OH species.

Stable catalysts are essential for the commercialization of DAFCs. Figure S2 shows the results of the aging test of the Pt/C and Pt/4CeO₂/C catalysts. For Pt catalysts, studies show that in the basic medium, specifically, the dissolution of Pt is greater than in the acid medium [40,41], under certain conditions, but other processes such as particle growth also lead to a more marked decrease in the ECSA in an alkaline medium [42]. It was possible to verify a loss of active area before and after the RPC (repetitive potential cycling) for Pt/CeO₂/C catalysts (Figure S2 in Supplementary Material), evidenced by the reduction of the hydrogen area, likely due to an increase in particle size, since no changes in the atomic ratio between Pt/CeO₂ (EDX before and after RPC, Table S1, in Supplementary Material) were observed. As can be seen in Table S1, the ECSA loss of ceria containing sample was lower than that of Pt alone, indicating the CeO₂ presence improve the stability of Pt particles. On the other hand, the RPC carried out in acid medium showed that after 1000 cycles total loss of CeO₂ occurs, demonstrating that the alkaline medium provides greater stability to CeO₂. The same Pt/CeO₂ atomic ratio before and after RPC indicates that no ceria loss took place.

3. Materials and Methods

The preparation of Pt and Pt/CeO₂/C electrocatalysts was carried out using the formic acid method [43]. The suspension of CeO₂ (Pangea International, 99.999%) was prepared, with the desired proportion, with hexachloroplatinic acid hexahydrate (Alfa Aesar[®]; 99.9% (Tewksbury, MA, USA), sonifying the mixture for 12 min. The suspension of the metal precursor with the rare earth was added slowly by dripping in the hot solution of formic acid (0.5 mol L⁻¹) with carbon Vulcan (previously treated at 850 °C/5 h), for 30 min at 80 °C, after cooling, then vacuum filtration was performed. The solid precipitate was rinsed with 500 mL of distilled water and dried in an oven at 80 °C for 2 h. The Pt/CeO₂/C were synthesized in the proportion 4, 6, and 8 wt% CeO₂. The three compartment electrochemical cell were utilized electrochemical measurements, with a Pt wire counter-electrode and Hg/HgO (0.1 mol L⁻¹) as reference electrode in 0.1 mol L⁻¹ NaOH solution. The electrocatalytic activity for EOR was performed in 0.1 mol L⁻¹ NaOH and 1.0 mol L⁻¹ EtOH, at 25 °C in Ar saturated solutions. The potential range was 0.05 to 1.00 V at 50 mV s⁻¹ for RPC used as the ageing test, applying 3000 cycles. In this case, EDX analyzes were made on the catalytic layer deposited on the electrode before and after the aging tests, a PINE removable carbon disk electrode was used.

The technique of X-ray Spectroscopy by Dispersive Energy (EDX), spectrometer Zeiss-Leica[®] 440 Electron Microscopy Inc., Thornwood, NY, USA, with a SiLi detector. Thermogravimetric analyzes (Mettler Toledo, Columbus, OH, USA) using synthetic air as a gas at a heating rate of 10 °C min⁻¹. The catalysts were analyzed by XRD (X-ray diffraction) using CuK α radiation (λ = 0.15406 nm) generated at 40 kV and 20 mA (RIGAKU-ULTIMA IV); 1° min⁻¹ for 2 θ between 20° and 90°. Transmission electron micrograph (TEM) analysis was carried out at 200 kV using a Philips CM 200 microscope. The XAS experiments were performed around the Pt L₃ edge (11564.25 eV). Experiments were carried out with 1000 accumulations with an exposure time of 150 ms. The measurements were carried out using a Spectro electrochemical cell was showed in Figure S3, in Supplementary Material. The catalysts loading was 4 mg Pt cm⁻².

4. Conclusions

The effect of ceria on the structural characteristics and the activity for EOR in alkaline medium of Pt/CeO₂/C catalysts, prepared by the formic acid method, was investigated. The presence of CeO₂ increased both the particle size and the d-band vacancies of platinum. The addition of ceria increased the activity towards EOR of platinum through the bifunctional mechanism, supporting the removal of Pt adsorbed CH₃CO by Ce adsorbed OH. On the other hand, the increase of Pt d-band vacancy with increasing CeO₂ content promoted

OH- adsorption on Pt atoms, blocking the active sites and hindering the EOR. The practical impact of these results on the preparation of Pt/CeO₂/C catalysts is to avoid the use of large amounts of ceria, in order not to nullify its positive effect on the electrochemical properties of platinum. Due to the counteracting effects, the EOR activity of Pt/CeO₂/C electrocatalysts show the best performance for the Pt:Ce atomic ratio of 4:1. Future research work should concern the refinement of the optimal amount of CeO₂, performing electrochemical measurements on Pt/CeO₂/C catalysts with ceria contents in the range 2–5%. Moreover, in order to evaluate their impact on the electrochemical performance, the same measurements should be carried out using different types of carbon supports, such as carbon nanotubes and graphene, and ceria with different particle size.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal11050579/s1>, Figure S1. Survey Spectrum of Pt/C and Pt-CeO₂/C catalysts, Figure S2. Cyclic voltammograms of Pt/4CeO₂/C and Pt/6CeO₂/C catalysts before and after RPC catalysts in 0.1 mol L^{−1} under Ar at room temperature and a scan rate of 50 mV s^{−1}, Figure S3. New design Spectro Electrochemical Cell. Table S1: Pt electrochemical surface area (ECSA) by CV and EDX composition of Pt/4CeO₂/C and Pt/6CeO₂/C catalysts before and after RPC. Protocol: Repetitive Potential Cyclic (RPC).

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